I. ENEDIOLS FROM HEXAISOPROPYLBENZIL
II. BIMOLECULAR REDUCTION OF MESITALDEHYDE

BY

EVAN CHARLES HORNING

B.S., University of Pennsylvania, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1940

URBANA, ILLINOIS
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PART I

ENEDIOLS FROM HEXAISOPROPYLBENZIL

Introduction

The preparation of the enediols from hexaisopropylbenzil was undertaken in order to determine the effect of increased steric hindrance on the properties of enediols. By analogy with the methyl and ethyl analogs it was to be expected that the new enediols would be more stable and hence more suitable for study than those hitherto available.

Experimental and Discussion of Results

The starting point for the synthesis of the enediol was 2,4,6-triisopropylbenzene, which was prepared through a Friedel-Crafts reaction. Bromination provided 2,4,6-triisopropylbromobenzene. The preparation of the corresponding Grignard reagent followed, and carbonation then resulted in the formation of 2,4,6-triisopropylbenzoic acid.

The acid was converted into the acid chloride by treatment with thionyl chloride in the cold. A reductive coupling of the acid chloride by the method employed by Fuson and Corse[1] using the binary mixture (magnesium and magnesium iodide) of Gomberg and Bachmann[2] provided a mixture of *cis*-1,2-di-(2,4,6-triisopropylphenyl)-acetylene glycol and 2,2′,4,4′,6,6′-hexaisopropylbenzil. Separation was accomplished by a selective solvent.

This enediol was a white solid, melting at 175-176° in a nitrogen-filled capillary. It was fairly stable in air but autoxidation became evident (appearance of the yellow benzil) within four or five hours. This stability is greater than that observed for the lower homologs.

Catalytic reduction of the benzil in methanol, a method used by Thompson,[3] was found to yield a mixture in varying proportions of *trans*-1,2-di-(2,4,6-triisopropylphenyl)-acetylene glycol and the *cis* form previously obtained, depending on the conditions imposed. A prolonged treatment provided the *trans* form in about 80 per cent yield. A drop or two of piperidine was bene-

ficial in promoting this effect. When a small amount of acetic acid (one-tenth of the solution volume) was added the reaction proceeded only to the *cis*-enediol. Limiting the acetic acid to catalytic amounts weakened this effect, and approximately equal quantities of *cis* and *trans* forms were obtained.

The *trans*-enediol was a white solid, melting at 259-260.5° in a nitrogen-filled capillary. It was much less soluble in the solvents employed than was the *cis* form. It was very stable in air, autoxidation being evident only after a period of several weeks.

It was found possible to effect a partial conversion of the *cis* form, obtained from a reduction with the binary mixture, to the *trans* isomer by prolonged contact with the platinum catalyst.

Treatment of the *trans*-enediol with acetic anhydride resulted in the formation of a diacetate which was also produced in small amount by a similar treatment of the *cis*-enediol. Catalytic reduction of the benzil in acetic anhydride yielded another diacetate identical with that produced by the action of acetic anhydride in pyridine on the *cis*-enediol.

Isomerization to the benzoin was accomplished by treating the *cis*-enediol with methanolic hydrogen chloride. The same treatment was without effect on the *trans*-enediol. This behavior is not characteristic of ordinary enol-keto tautomerization.

The dimethyl ether of the *cis*-enediol was prepared through the magnesium salt and methyl sulfate. Similar treatment of the *trans*-enediol resulted only in oxidation. The resistance of the ethylenic bond to hydrogenation was evidenced by the failure of the ether to take up hydrogen in the presence of Raney nickel at 175°; also, the diketone was not reduced to the glycol with a copper chromite catalyst at 200°.

Summary

Both *cis* and *trans* modifications of the enediol from hexaisopropylbenzil have been prepared. The *cis* form is stable for a few hours in air, while the *trans* form suffers appreciable autoxidation only in a period of several weeks.

It has been demonstrated that catalytic reduction of the diketone may be made to yield either isomer, depending upon

the conditions imposed. Acetic acid promoted reduction to the *cis* form. The partial conversion of *cis* to *trans* under the influence of a platinum catalyst was shown.

Two isomeric diacetates of the enediols have been prepared, each in two different fashions.

Isomerization of the *cis*-enediol to the benzoin was accomplished by the use of hydrogen chloride in methanol. Similar treatment of the *trans*-enediol was without effect.

A diether of the *cis* enediol was prepared, and the resistance of the ethylenic bond to hydrogenation was shown.

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PART II

BIMOLECULAR REDUCTION OF MESITALDEHYDE

Introduction

Bimolecular reduction of aldehydes leads to the formation of glycols. This type of reduction has been applied to mesitaldehyde, and an incidental study of the aldehyde has been carried out.

Experimental and Discussion of Results

The preparation of mesitaldehyde by the use of the Grignard reagent and ethyl formate[1] was investigated and found to yield both mesitaldehyde (33 per cent yield) and mesitylene. The course of the reaction was only slightly dependent on the temperature. The method, however, was not well adapted to the laboratory production of moderate amounts of material.

An investigation of other aromatic aldehyde syntheses led to the development of a modified Gattermann reaction which allowed the easy production of the aldehyde from mesitylene in 76 per cent yield. Zinc cyanide was used as the source of the hydrogen cyanide required, and tetrachloroethane was employed as a solvent.

The bimolecular reduction of benzaldehyde with the binary mixture, magnesium and magnesium iodide, results in the forma-

tion of benzoin and benzyl alcohol, but a hydrobenzoinate salt is present as an intermediate.[2] It was thought that the corresponding hydromesitoinate salt might be more resistant to oxidation and hence would allow the isolation of some hydromesitoin. When this reaction was applied to mesitaldehyde it was found that hydromesitoin was one of the products. Another of the products was *s*-dimesitylethylene. A third substance obtained from the reaction was apparently a mixture of hydromesitoin and some other material, since acetylation produced a small amount of hydromesitoin diacetate. Oxidation of this substance with chromic anhydride yielded mesitoic acid; reduction with phosphorus and iodine yielded *s*-dimesitylethane.

The bimolecular reduction of mesitaldehyde with a zinc-copper couple was effected, but the course of the reaction was found to be dependent on the conditions. The use of aqueous ethanol and acetic acid brought about reduction to hydromesitoin. A change of solvent to methanol, retaining, however, the acetic acid, resulted in the formation of mesitylcarbinol.

Summary

Mesitaldehyde was prepared from mesitylmagnesium bromide and ethyl formate in 33 per cent yields. Mesitylene was also a product of the reaction.

A modification of the Gattermann reaction was developed which gave mesitaldehyde in 76 per cent yield.

The bimolecular reduction of mesitaldehyde with the binary mixture, magnesium and magnesium iodide, was found to yield hydromesitoin, *s*-dimesitylethylene, and a solid which has not been identified. It appears to be a mixture of hydromesitoin and some other compound, since acetylation gave hydromesitoin diacetate as one product.

The bimolecular reduction of mesitaldehyde with the zinc-copper couple resulted in the formation of hydromesitoin, but it was found that a change of solvent diverted the reaction and gave mesitylcarbinol.

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VITA

The writer was born in Philadelphia, Pennsylvania, on June 6, 1916. He attended the public schools of that city until 1933 when he entered the University of Pennsylvania. He was granted the degree of Bachelor of Science in Chemical Engineering in 1937, and in the fall of the same year he entered the graduate school of the University of Illinois as a teaching assistant in organic chemistry. He held a University fellowship during 1938-1939 and the du Pont fellowship during 1939-1940.